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Technical Report #2

"Isothermal Compressiblity of SPC/E Water"

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ABSTRACT

Molecular dynamics computer simulations on rigid SPC/E water molecules were performed. The goal of the simulations is to study the behavior of isothermal compressibility, which was calculated in the simulations at T=298, 273 and 248K. The calculated isothermal compressibilities at these temperatures display a trend contrary to the experimental observations. The hydrogen bonded network in water was also investigated. No correlation between the temperature dependence of isothermal compressibility and the number of hydrogen bonded pentagons was observed.

Key words: Molecular dynamics computer simulation, isothermal compressibility, Thermodynamics, Network, Fluctuations, Water.

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ISOTHERMAL COMPRESSIBILITY OF SPC/E WATER

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Abstract

Molecular dynamics computer simulations on rigid SPC/E water molecules were performed. The goal of the simulations is to study the behavior of isothermal compressibility, which was calculated in the simulations at T=298, 273 and 248K. The calculated isothermal compressibilities at these temperatures display a trend contrary to the experimental observations. The hydrogen bonded network in water was also investigated. No correlation between the temperature dependence of isothermal compressibility and the number of hydrogen bonded pentagons was observed.

I. Introduction

Among many unusual features displayed by liquid water the anomalous behavior of thermodynamic response functions is one of the most interesting. The anomaly in the behavior of the response functions such as constant pressure heat capacity (C_p), thermal expansivity coefficient (α_T) and isothermal compressibility (κ_T), especially at temperatures below 0°C is believed to be due to the onset of some sort of cooperative phenomena, implying the possible presence of anomalous fluctuations in density [1]. Since the isothermal compressibility κ_T is a direct measure of density fluctuations we shall concentrate our attention on this quantity. While for most of the liquids κ_T decreases when the temperature decreases, for liquid water κ_T displays a minimum at $T \approx 50°C$. Below this temperature κ_T rises, especially very rapidly in the supercooled region. The described anomalous behavior of the compressibility is attributed to the superposition of "normal" fluctuations and anomalous fluctuations, that diverge at temperature T_S [2]. The nature of these anomalous fluctuations and their divergence at T_S is not clear.

Several theoretical models try to explain these anomalous density fluctuations. Stanley and Teixeira [3] ascribe the cooperative nature of the anomalous fluctuations to the clustering of fourfold hydrogen bonded water molecules. The patches of such clusters are characterized by local order and reduced local density. The Stanley-Teixeira model is a percolation model with the percolation threshold for fourfolded molecules achieved at T_S. Another model is due to Stillinger [4], who proposed the existence of a significant concentration of bulky unstrained polyhedra in water. The cooperativity of the fluctuations is again due to the geometry; for example a pair of dodecahedra can be stabilized by sharing the common pentagonal face. The model of Speedy [5] is similar to Stillinger's. While Stillinger does not specify the particular polygonal structure, Speedy concentrates his attention on pentagonal hydrogen bonded rings. These rings, according to Speedy, have a tendency to self replicate, thus generating low density patches. In Speedy's model the

density fluctuations grow proportionally to the number of five-membered hydrogen bonded rings until the limit of stability is approached at T_S.

From the outset, computer simulations helped us to choose among the competing theories, proposed to explain the experiment. Thus the first molecular dynamics simulation of water by Rahman and Stillinger [6] clearly displayed that water is correctly described by a distorted hydrogen bonding network or "continuum" model and not by its rival the mixture/interstitial model. One may also hope that computer simulations will assist us in determining which model among the three described above can explain the nature of anomalous fluctuations in density. Indeed, simulations that address the question of the nature of density fluctuations at low temperature are found in the literature. The results are controversial at least. To support Stanley and Teixeira's theory Geiger and Stanley performed a MD simulation on ST2 water [7], in which they observed the existence of low-density patches of water molecules [8]. Rapaport performed a MD simulation of MCY water [9] at -22°C and did not observe any correlation between local density and the number of hydrogen bonds associated with each water molecule [10]. Speedy and Mezei in their work aimed to support Speedy's theory reported an increase in five-member rings concentration with the temperature decrease [11]. Therefore they concluded that water anomalies may be related to self-replicating propensity of pentagons. The problem with their analysis is that they have correlated the increase in pentagon concentration observed in "computer" water with the increase in the compressibility in "real" water. But what if the compressibility of the "computer" water (which of course may depend on the model used in the simulation) is not increasing when temperature is decreased? To reach definite conclusions on the correlation between the polygon concentration increase and compressibility increase, one has to calculate the compressibility of the "computer" water. We know of only one study where the direct calculation of compessibility and its temperature dependence was performed. This was done by Jorgensen and Madura in their

Monte Carlo simulation performed on TIP4P potential [12]. The reported values for κ_T in [12] are: 67 ± 13 x 10^{-11} Pa^{-1} at T = 25°C (the experimental value is 45.2 x 10^{-11} Pa^{-1}), 24 ± 3 x 10^{-11} Pa^{-1} at T = 0°C (50.9 x 10^{-11} Pa^{-1} in experiment) and 23 ± 3 x 10^{-11} Pa^{-1} at T = -25°C (70.9 x 10^{-11} Pa^{-1} in experiment). One can see that according to ref. [12], κ_T for TIP4P water does not behave in the right way. The wrong behavior is also observed for C_p. The problem may be with TIP4P potential, but most probably it is in the length of the simulation. The simulation was performed under constant pressure and temperature conditions and the values of response functions C_p and κ_T were calculated using fluctuation formulas. To get good quantitative numbers using fluctuation formulas one needs very long simulations. In this respect calculations of C_p or κ_T are similar to the calculation of dielectric constant ϵ, which is known to require a very long simulation time [13]. To avoid very long simulations one can use the thermodynamic definition of the response function. In this case, to find κ_T from the computer experiment one has to determine that portion of the isotherm where one is interested in its slope. That can be obtained from 2 or 3 relatively short simulations. In what follows we describe such simulations and present the values of isothermal compressibility for SPC/E water [14] at three different temperatures. We also discuss the connection between the compressibility behavior and the concentration of five membered hydrogen-bonded rings in water structure.

II. Molecular Dynamics Simulations

Six molecular dynamics simulations in a canonical N,V,T ensemble and one simulation in N,P,T ensemble were performed. For N,V,T ensemble two simulations were performed at T=248 K, two simulations at T=273 K and two simulations at T=298 K. For the canonical ensemble simulations at every temperature one simulation was performed at the density roughly corresponding to 1 g/cc and at pressure around 1 atm., and the second simulation at the elevated density and elevated pressure. Every simulation was of 60 ps duration time, 20 ps were used for equilibration and the remaining 40 ps were used for

analysis. The 40 ps were divided into two blocks of 20 ps each and the average pressure over this block of time was calculated. Only one N,P,T simulation was performed at T=248 K. This simulation was done for longer duration, 400 ps, so that we can use the fluctuation formula for compressibility calculation.

The maintenance of a constant temperature and/or pressure in the system was achieved by an application of a Ferrario-Ryckaert algorithm [15], based on the extended variable method of Andersen [16] and Nose [17]. To find the values of the inertial parameters W_s and W_Q that drive the fluctuations in temperature and volume, several trial simulations were performed. We finally settled for values W_s = 100 (kJ/mol)ps^2 and W_Q =250 (kJ/mol/nm^6)ps^2, since these were the values that produced the most stable molecular dynamics. The potential energy of interaction between two water molecules was multiplied by the switching function proposed by Steinhauser [18], which smoothly reduces the energy from its value at R_T=0.8075 nm to zero at R_C=0.85 nm., the long-range forces contribution was taken into account by usage of the reaction field method. The dynamics was carried out on 216 molecules with the use of the Verlet algorithm [19] and the SHAKE procedure [20]. The time step was 2.5 fs and every fourth configuration was saved. The water model used in the simulations was SPC/E model. It was recently shown that this model in a nice way reproduces many of the features of bulk water [14,21].

III. Results and Discussion

a. Compressibility Calculation

The canonical N,V,T simulations were very similar to the ones recently performed in the study of pressure dependent properties of TIP4P water [22]. As in the simulation with TIP4P water the present simulation displays the weakening of the tetrahedral order taking place in water with the density increase. This is revealed by a diminished intensity of the first peak and by gradual disappearance of the second peak with the density

increase, illustrated in figure 1 for T=248 K.

To calculate the compressibility κ_T we used the finite difference approximation, i.e.

$$\kappa_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial p}\right)_T \approx \frac{\Delta \ln\rho}{\Delta p} = \frac{\ln\rho_2/\rho_1}{P_2\text{-}P_1} \qquad (1)$$

The linear approximation in (1) is expected to be good for water in the region 0-2000 atmospheres, since the isotherm for real water is nearly linear in this region. In equation (1) ρ_1 is the density corresponding to pressure P_1 and ρ_2 is the density corresponding to P_2. These values of ρ and P were obtained from molecular dynamics runs at three different temperatures. To enrich the statistics every run was divided into two blocks and for every block the values of P were calculated. This helps to explain the notation used in Table 1. Thus P_{11} means pressure P_1 corresponding to density ρ_1, P_{12} is the pressure corresponding to density ρ_1 in the second half of the run, P_{21} is the pressure corresponding to density ρ_2 from the first half of the run, etc. Such scheme permits us to calculate four possible values for the isothermal compressibility κ_T at each temperature. The values of these four quantities are given in Table 1 together with the average value.

We have also used the N,P,T ensemble to calculate the compressibility of water. Since this is done through the fluctuation formula, $\kappa_T = <\Delta V^2>/Vk_BT$, it demands long simulation times. We watched the time dependence of the cumulative value of κ_T and when it reached a plateau value at $\kappa_T \approx 35.5\text{x}10^{-11}$ Pa^{-1} after around 400 ps the simulation was terminated. The cumulative behaviour of κ_T is shown in Fig. 2. To obtain an idea of the error in κ_T present in this simulation we divided 400 ps into three blocks 200 ps each (0-200ps, 100-300ps and 200-400ps). The values of of κ_T for each block and the average value are given in Table 1. As one can see the values of κ_T obtained from N,P,T and N,V,T simulations show rather good agreement between themselves. The calculated values for the isothermal compressibility display a slight minimum around T≈273K, similar

to the one found experimentally at T≈323K. This behavior is contrary to experimental observation that isothermal compressibility monotonically increases and nearly doubles its value when the temperature is lowered from T = 298K to T = 248K. It is therefore possible that the thermodynamic properties of a "computer" water are shifted down in temperature. Such downshift was for example found for TIP4P water, which is estimated to have a melting temperature somewhere around 240K [24]. We do not know what is the melting point of SPC/E water, but it is possible that it is also shifted down in temperature.

To see if there is any correlation between the observed behavior of κ_T and the concentration of pentagons in water we performed a topological analysis of SPC/E water structure, which we describe below.

b. Hydrogen Bonds and Their Network

To investigate underlying geometrical structures in further detail, we have enumerated distribution of hydrogen bonds and non-short-circuited polygons formed by the hydrogen bonds. Our calculation is based on a set of 100 equidistant configurations taken from the final 20ps run at lower density (ρ_1) at each temperature. In our simulation a pair of molecules is considered hydrogen bonded if they are within 0.32 nm away (roughly first minimum of the oxygen-oxygen radial distribution) and their interaction energy falls below the cutoff, V_{HB} = -2.5 Kcal/Mole. The results for the hydrogen bond distribution are displayed in Table 2. The distribution at T=298 K agrees quite well with previous findings [23]. As expected, the concentration of four-bonded molecules considerably increases as temperature is decreased.

To calculate the ring distribution we have followed the definition of non-short-circuited polygons as described by Rahman and Stillinger [25], viz, no two vertices of polygon are connected by shorter number of bonds than the minimum number of bonds already existing within the polygon. In conformity with their concern about the erronious

polygon closures due to the small number of molecules (216) used in the simulation, we have used eight replicas of the MD cells to construct a 2x2x2 larger cube containing 1728 distinct molecules under periodic boundary conditions for the purpose of the polygon enumeration.

We have used the following polygon enumeration algorithm which is similar to the triplet counting algorithm developed by Belch and Rice [26]. In this scheme for a given configuration we first generate a list of bonded neighbors for each molecule. A molecule is considered for polygon search only if it has at least two bonded neighbors. For a given molecule designated as 'B' we arbitrarily designate its two neighbors as 'A' and 'C'. We start the search by looking into the neighbors of 'C'. If 'A' is a neighbor of 'C' then we conclude ABC is a triangle. If triangles are not found then subsequent neighbors are searched to find polygons of larger sizes. For each triplet of molecule only the shortest non-short-circuited polygon is listed. After exhaustively searching through all the molecules using all distinct triplets and enumerating all the polygons of different sizes a final search is performed to identify duplicates as well as short circuiting of larger polygons by smaller ones.

Using the above scheme, we have exhaustively identified all possible non-short-circuited polygons of sizes 3 through 11. We did not look for larger size polygons since it would consume prohibitive computer time and also not very pertaining to our present study. In Table 3, we show the distribution of hydrogen bonded polygons at three temperatures we have studied. Although pentagons increases in number with temperature decrease the predominance of hexagons becomes more pronounced at lower temperature indicating a competition between nucleation process and retention of liquid structure.

IV Conclusions

Our study of hydrogen bonded network in SPC/E water demonstrates that temperature decrease does not produce a structure where five-membered rings are dominant. As a matter of fact, six membered rings remain dominant and the rate of their increase is parallel to the rate of the increase in number of five-membered rings. Similar behavior was recently observed in the simulation performed on ST2 water by Mausbach, Schnitker and Geiger [27]. We agree with their conclusion that the observed structural changes due to the temperature decrease can be attributed to the approach of the amorphous structure. In this structure hydrogen bonded rings of all sizes are expected. Moreover, a lack of correlation between the behavior of the calculated isothermal compressibility and the number of five-membered rings indicates that Speedy's hypothesis may not be right. We also would like to point out, that while an effective pair-potential used in the simulations with SPC/E water is rather successful in reproducing many properties of liquid water, it fails to reproduce the anomalous behavior of isothermal compressibility in temperature range 298K-248K. It would be interesting to see if polar-polarizable models of water, which are now under investigations [28,29], demonstrate the anomalous behavior of thermodynamic response functions in this temperature range. Note that recently designed random network models also are not able to reproduce the anomalous behavior of the isothermal compressibility [30,31]. We hope that future computer studies of low temperature behavior of water will help to resolve the nature of the anomalous fluctuations responsible for anomalous behavior of the response functions.

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Legends for Tables :

1. Isothermal compressibility of SPC/E water. Density (ρ in gm/cc), pressure (P in atm) and compressibility (κ in 10^{-11} Pa^{-1}) calculated from 20 ps blocks are shown for NVT ensemble. Compressibility using NPT ensemble at 248 K is also shown.

2. Distribution of hydrogen bonds per molecule in SPC/E water at three different temperatures. The average number of hydrogen bonds per molecule is given in the last row.

3. Distribution of hydrogen bonded polygons in SPC/E water and their temperature dependence. The actual number of rings alongwith their uncertainties are shown.

Legends for Figures :

1. The effect of pressure on oxygen-oxygen radial distribution at 248 K in NVT ensemble. The solid line is at lower density (1.00722 g/cc) and the dotted line is at higher density (1.0822 g/cc).

2. Cumulative plot of isothermal compressibility versus time at 248 K in NPT ensemble.

TABLE 1

T	248K	273K	298K
ρ_1	1.0072	1.0055	1.0033
P_{11}	25.39	-280.42	278.08
P_{12}	-68.58	-30.27	207.94
ρ_2	1.0822	1.0755	1.0550
P_{21}	1779.97	1762.16	1450.79
P_{22}	1790.14	1698.72	1385.60
κ_{11}	39.58	31.86	41.43
κ_{12}	39.35	32.88	43.87
κ_{21}	37.57	36.31	39.05
κ_{22}	37.36	37.63	41.25
κ_T(NVT)	38.47 ± 1.16	34.67 ± 2.74	41.41 ± 1.95
κ_T(NPT)	34.07 ± 5.21		

TABLE 2

n_b	248K	273K	298K
0	0.00005	0.0001	0.00097
1	0.0038	0.0088	0.0153
2	0.0546	0.0922	0.1198
3	0.2918	0.3486	0.3859
4	0.6091	0.5072	0.4362
5	0.0403	0.0425	0.0411
6	0.0003	0.0006	0.0007
$<n_b>$	3.63	3.48	3.37

TABLE 3

	$N_j(T)$		
j	248K	273K	298K
3	2.1 ± 2.22	2.6 ± 2.22	3.3 ± 2.38
4	19.7 ± 4.78	20.7 ± 5.03	18.4 ± 5.31
5	80.2 ±12.62	62.6 ±10.40	54.9 ±11.09
6	106.7 ±14.47	79.2 ±13.96	62.5 ±11.92
7	87.6 ±12.26	77.4 ±15.23	61.4 ±12.15
8	52.6 ± 9.45	49.1 ± 9.78	47.0 ±10.25
9	26.1 ± 7.70	31.8 ± 7.35	33.5 ± 7.35
10	8.1 ± 4.67	15.2 ± 5.62	20.1 ± 5.51
11	2.0 ± 2.21	6.1 ± 3.60	9.5 ± 4.62

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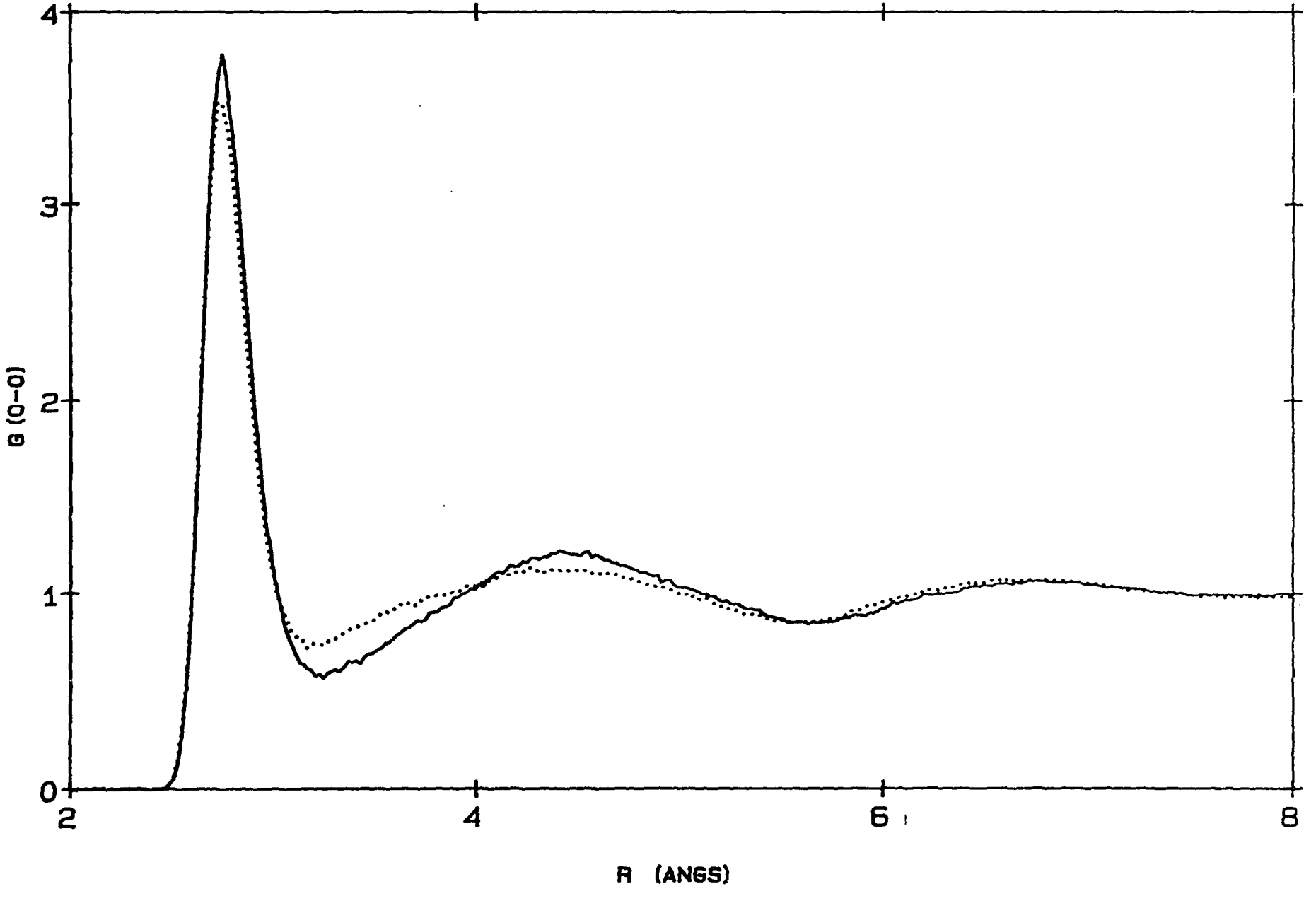

Figure 1

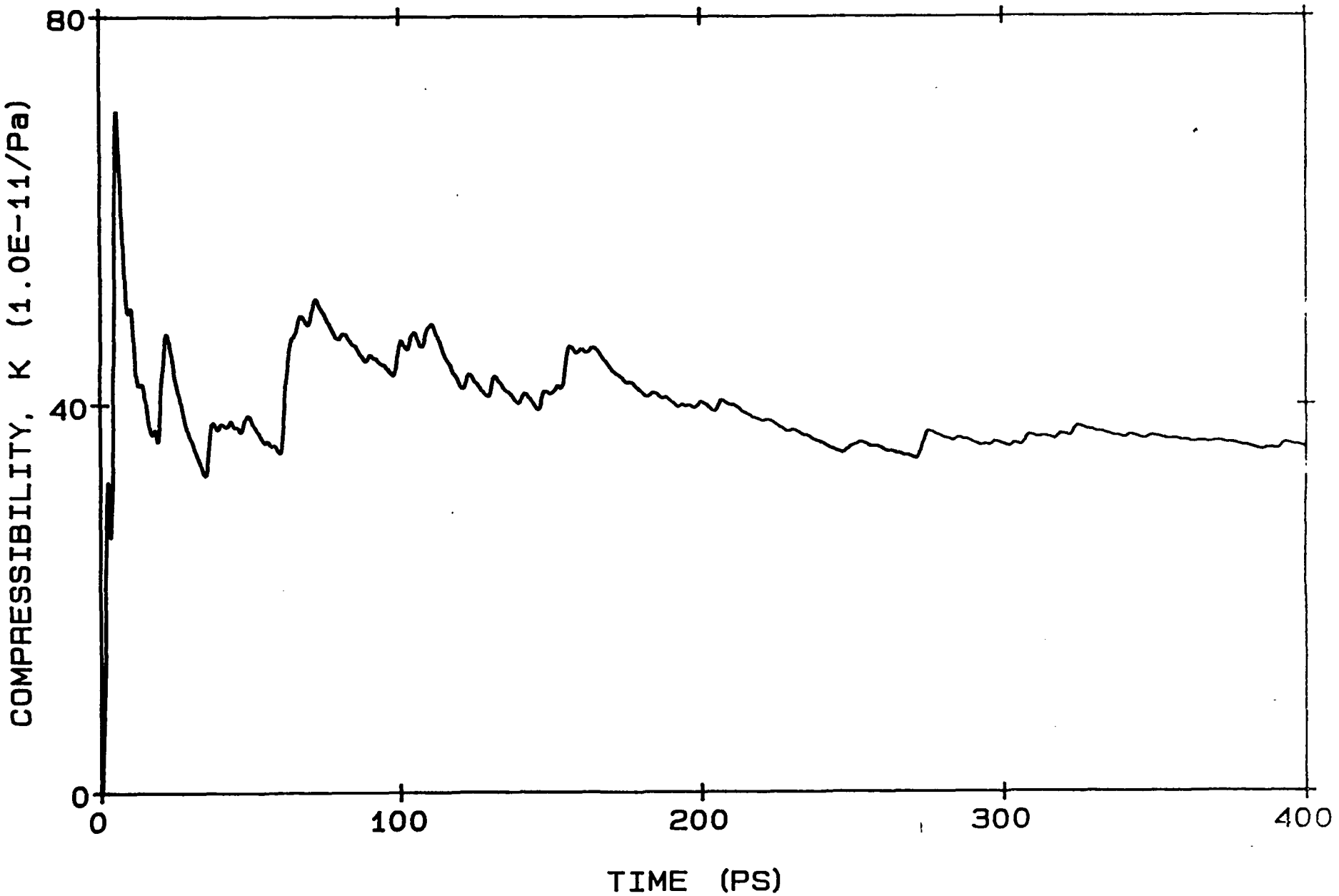

Figure 2